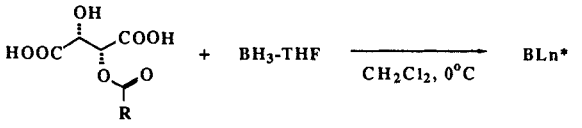
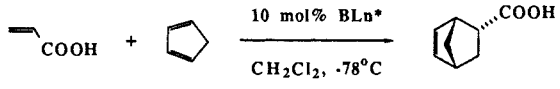
of our initial investigation that demonstrate for the first time the possibility of achieving useful enantioselectivities with a simple chiral controller ligand, easily obtainable in either enantiomeric form from inexpensive tartaric acid.

Reaction of the monoacylated tartaric acid (**1a-d**)[5] with 1 equiv of borane–THF complex in dichloromethane at 0 °C should result in the formation of a chiral acyloxyborane intermediate. Acrylic acid (10-fold excess) was added to this catalyst solution at 0 °C, and then the mixture was cooled to −78 °C. To this was added cyclopentadiene, and the resulting mixture was stirred at the same temperature for 24 h. After usual workup and chromatographic separation, Diels–Alder adduct was isolated in 93% yield (mixture of endo and exo isomers in the ratio of 96:4). The product mixture was subjected to iodolactonization, and the major endo isomer was separated as iodolactone.[6] The product showed a specific rotation ($[\alpha]_D$) of −86°, which corresponded to 78% optical yield with *R*-configuration.[7] The use of the D-tartaric acid should afford the enantiomer of the adduct. In fact, *S*-isomer was obtained from the unnatural form of tartaric acid in 85% yield and 78% ee. The reaction seems to be general and applicable to other dienes and unsaturated acids.[8] The extent of asymmetric induction largely depended on the acyl moiety of tartaric acid derivatives, and **1d** revealed the highest asymmetric induction among the tartaric acid derivatives tested so far.[9]



1a: R = CH_3
b: R = t-Bu
c: R = Ph
d: R = 2,6-$(MeO)_2$Ph



	Yield(%)	ee(%)
2a:	66	34
b:	68	51
c:	88	35
d:	93	78

We believe that the experimental results gained in this work will stimulate further exciting advances in this important area of chemistry. At present, the mechanism of asymmetric induction is not clear, but it may be supposed that α-hydroxy acid and borane make the rigid cyclic structure to form effective asymmetric field.[10] Many applications of this new catalytic methodology in synthesis can be foreseen.

Acknowledgment. Support of this research by the Ministry of Education, Science and Culture, Japanese Government is gratefully acknowledged.

(4) For the asymmetric Diels–Alder reaction of chiral ester or analogues, see: (a) Paquette, L. A. In *Asymmetric Synthesis, Vol. 3*; Morrison, J. D., Ed.; Academic Press: Orlando, FL, 1984. (b) Helmchen, G.; Karge, R.; Weetman, J. In *Modern Synthetic Methods, Vol. 4 • 1986*; Scheffold, R., Ed.; Springer-Verlag: Berlin, Heidelberg, 1986. (c) Oppolzer, W. *Tetrahedron* **1987**, *43*, 1969. Recently, some catalytic processes using chiral Lewis acid have been explored: (d) Hashimoto, S.; Komeshima, N.; Koga, K. *J. Chem. Soc., Chem. Commun.* **1979**, 437. (e) Bednarski, M.; Maring, C.; Danishefsky, S. *Tetrahedron Lett.* **1983**, *24*, 3451. (f) Kelly, T. R.; Whiting, A.; Chandrakumar, N. S. *J. Am. Chem. Soc.* **1986**, *108*, 3510. (g) Narasaka, K.; Inoue, M.; Okada, N. *Chem. Lett.* **1986**, 1109. (h) Maruoka, K.; Sakurai, M.; Fujiwara, J.; Yamamoto, H. *Tetrahedron Lett.* **1986**, *27*, 4895. (i) Narasaka, K.; Inoue, M.; Yamada, T. *Chem. Lett.* **1986**, 1967. (j) Bir, G.; Kaufmann, D. *Tetrahedron Lett.* **1987**, *28*, 777. (k) Quimpere, M.; Jankowski, K. *J. Chem. Soc., Chem. Commun.* **1987**, 676. (l) Chapuis, C.; Jurczak, J. *Helv. Chim. Acta* **1987**, *70*, 436. (m) Seebach, D.; Beck, A. K.; Imwinkelried, R.; Roggo, S.; Wonnacott, A. *Helv. Chim. Acta* **1987**, *70*, 954. (n) Takemura, H.; Komeshima, N.; Takahashi, I.; Hashimoto, S.; Ikota, N.; Tomioka, K.; Koga, K. *Tetrahedron Lett.* **1987**, *28*, 5687. (o) Narasaka, K.; Inoue, M.; Yamada, T.; Sugimori, J.; Iwasawa, N. *Chem. Lett.* **1987**, 2409. (p) Maruoka, K.; Itoh, T.; Shirasaka, T.; Yamamoto, H. *J. Am. Chem. Soc.* **1988**, *110*, 310.

(5) These compounds were prepared by the monoacylation of dibenzyl tartrate followed by hydrogenolysis.

(6) Berson, J. A.; Ben-Efraim, D. A. *J. Am. Chem. Soc.* **1959**, *81*, 4083. No recrystallization of the product was conducted.

(7) Kirmse, W.; Siegfried, R. *J. Am. Chem. Soc.* **1983**, *105*, 950.

(8) For a preliminary experiment, the reaction of crotonic acid and cyclopentadiene with this catalyst at −20 °C gave the Diels–Alder adduct of 60% ee. Acrylic acid also reacted with 2,3-dimethyl-1,3-butadiene under the similar reaction conditions to afford the adduct of 55% optical purity. The detailed results will be published in full.

(9) The appropriate designing of the chiral tartaric acid ligands should reach to the satisfactory level of asymmetric synthesis.

(10) The possibility for the existence of oligomeric or polynuclear species cannot be ruled out. See: Pedersen, S. F.; Dewan, J. C.; Eckman, R. R.; Sharpless, K. B. *J. Am. Chem. Soc.* **1987**, *109*, 1279.

Syndiospecific Propylene Polymerizations with Group 4 Metallocenes

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Received May 13, 1988

Isotactic polypropylenes have been synthesized in stereospecific group 4 metallocene polymerizations. Stereochemical control by chiral growing chain ends and by enantiomorphic sites led to two different isotactic polymer configurational microstructures.[1,2]

Partially syndiotactic polypropylene has been obtained in vanadium-catalyzed polymerizations below −50 °C. The polymer ...rrrrrmrrrrr... stereosequences are in accord with chain end stereoregulation.[3]

In this contribution we describe new syndiospecific polymerizations with Hf and Zr metallocenes yielding crystalline polymer in high yields at conventional polymerization conditions. The polymer configurational microstructure is consistent with site control and with the active sites isomerizing with each monomer addition.

Metallocenes. The molecular structure and atom numbering scheme of isopropyl(cyclopentadienyl-1-fluorenyl)hafnium(IV) dichloride (i-PrCp-1-FluHfCl_2) is displayed in Figure 1. The crystal structure reveals a bent, sandwich complex with trihapto bonding of the fluorenyl ligand to hafnium. The complex is prochiral, C(2) and C(5) in the C5 fluorene ring are chiral and of opposite handedness, and the hydrocarbon ligand system is stereorigid.[4,5]

Polymerizations. Schering's methylalumoxane was used to alkylate and, possibly, produce brightly colored violet Zr and pink Hf active cations.[1] The catalysts were precipitated at 25 °C with liquid propylene and prepolymerized for 3 min while heating to the polymerization temperatures. This procedure resulted in uniformly sized, symmetrical, free flowing, granular polymer

(1) Ewen, J. A. *J. Am. Chem. Soc.* **1984**, *106*, 6355–6364.

(2) Ewen, J. A.; Haspeslagh, L.; Atwood, J. L.; Zhang, H. *J. Am. Chem. Soc.* **1987**, *109*, 6544–6545.

(3) Zambelli, A.; Locatelli, P.; Provasoli, A.; Ferro, D. R. *Macromolecules* **1980**, *13*, 267.

(4) The ligand was synthesized from stoichiometric reaction of fluorenyllithium salt and 6,6-dimethylfulvene in THF. The bright yellow hafnium and the deep red zirconium complexes were isolated by crystallization at −20 °C after warming the ligand dianion and a slurry of MCl_4 in CH_2Cl_2 from −78 °C to 25 °C.

(5) The space group for i-PrCp-1FluHfCl_2 is $P2_1/c$ (no. 14) with a = 10.66 (1) Å, b = 8.878 (5) Å, c = 18.59 (2) Å, β = 100.51 (9)°, V = 1729 (3) Å^3, Z = 4, and D_{calcd} = 1.996 g/cm^3. Refinement on the 1614 data $I > 3.00(I)$ resulted in residuals R = 0.058 and R_w = 0.060.

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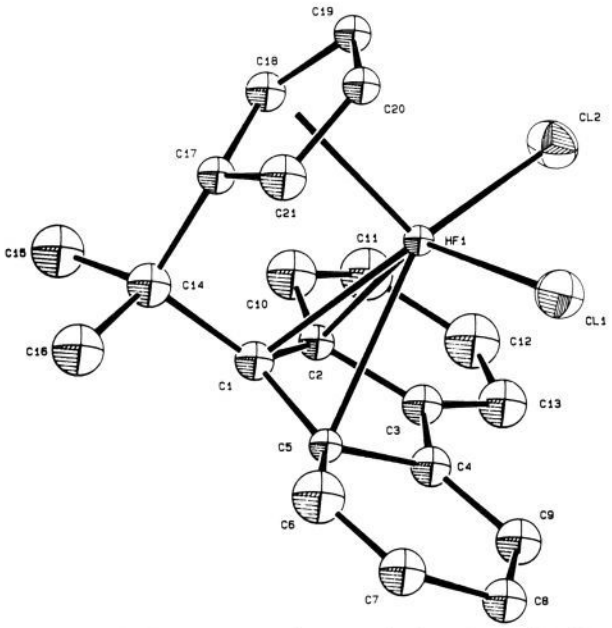


Figure 1. Molecular structure and atom numbering scheme of i-Pr[Cp-1-Flu]$HfCl_2$. The atoms are represented by their 50% probability ellipsoids. Important interatomic distances (Å) and bond angles (deg) are as follows: Hf–Cl(1), 2.391 (6); Hf–Cl(2), 2.394 (6); Hf–C(1), 2.40 (2); Hf–C(2), 2.49 (2); Hf–C(3), 2.64 (2); Hf–C(4), 2.64 (2); Hf–C(5), 2.57 (2); Hf–CEN(Flu), 2.24; Hf–CEN(Cp), 2.16; CEN(Flu)–Hf–CEN(Cp), 119.4; C(1)–C(14)–C(17), 101.1. (CEN denotes centroid of a C-5 ring.)

Table I. Conditions and Results for Syndiospecific Polymerizations[a]

transition metal, (μmol)	pol. temp, °C	time, min	yield, g	$10^{-3}\cdot\bar{M}_w$	$\bar{M}_w/\bar{M}_n$	rrrr
Zr (1.3)	25	60	26	133	1.9	0.86
Zr (1.3)	50	25	162	69	1.8	0.81
Zr (1.2)	60	60	185	52	1.8	
Zr (1.2)[b]	70	60	158	55	2.4	0.76
Hf (19.2)	50	30	27	777	2.3	0.74
Hf (5.8)	70	60	96	474	2.6	

[a] Propylene (1.2 L); 10 mL of 10.7 wt% methylaluminoxane (MAO) obtained from Shering Industrie-Chemikalien with MW = 1300. [b] MAO (5 mL).

particles with 0.5 g/mL bulk density at 70 °C polymerization temperature. Additional polymerization results are summarized in Table I.

Polymer C-13 NMR Analyses. The Zr produced polymers have a ...rrrrrmmrrrrrmrrrrrmmrrrrr... microstructure with the isotactic triads being the predominant stereochemical defect. The ... rrrrmmrrrr... stereosequences indicate site stereochemical control with chain migratory insertions resulting in site isomerizations and occasional reversals in diastereoface selectivity (Scheme I).[6] Catalyst isomerizations independent of monomer addition would result in the meso dyads.

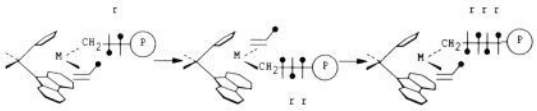
Two percent of the polymer obtained with Hf consists of isotactic blocks. The ...rrrrrrrrmmmmmrrrrrrrr... stereoblock microstructure or the isotactic/syndiotactic mixtures are attributed to syndiospecific contact ion pairs and associated neutral, isospecific complexes.

Concluding Remarks. The polymerization rates and the polymer molecular weights obtained with the syndiospecific Zr complexes are higher than those obtained with isospecific analogues.[2] The syndiospecific complexes are stereospecific over a wide range of

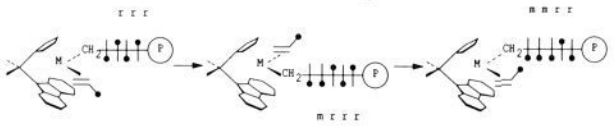
(6) C-13 NMR analysis of a sample with $\bar{M}_n$ = 4800 (GPC) and produced with 100 mg of i-PrCp-1-Flu$ZrCl_2$ and 5 mL of MAO at 80 °C in pentane at 20 psi propylene showed isopropyl (1.03%), vinylidene (0.51%), and *n*-propyl (0.53%) chain end groups. The absence of vinyl chain ends and the vinylidene chain end groups in a stereoregular environment consistent with the pentad analysis shows that the polymerizations proceed by a 1,2-insertion mechanism as indicated in Scheme I.

Scheme I

Syndiotactic Propagation



Reversed Diastereoface Selectivity



polymerization temperatures (Table I), and the "as-polymerized" samples contain little or no atactic polymer under very pure polymerization conditions.

The morphology of the polymer particles indicates the catalysts are propylene insoluble, heterogeneous systems. The narrow polydispersities are typical of chemically homogeneous, active species.

Supplementary Material Available: The ligand and metallocene synthetic procedures, polymerization procedure and listings of crystal data, atomic coordinates for hydrogen atoms, bond distances and angles, geometry for the hafnium atoms, best planes, and drawings of the unit cell (48 pages); listing of observed and calculated structure factors (21 pages). Ordering information is given on any current masthead page.

Correlation of Carbon-13 and Nitrogen-15 Chemical Shifts in Selectively and Uniformly Labeled Proteins by Heteronuclear Two-Dimensional NMR Spectroscopy

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Received May 11, 1988

Two-dimensional (2D) carbon-13 nitrogen-15 heteronuclear single-bond correlation [$^{13}C|^{15}N$]HSBC] spectroscopy[1] has been developed and applied to two double-labeled proteins. The approach has been used with *Streptomyces* subtilisin inhibitor (SSI), a homodimeric protein of reduced molecular mass (M_r) 23 000/dimer, labeled uniformly with 60% nitrogen-15 and labeled specifically to 60% carbon-13 at the carbonyl carbons of the three methionine residues,[2] and with *Anabaena* 7120 flavodoxin, a

(1) Successful implementation of $^{13}C|^{15}N$]HSBC has been reported recently for ^{15}N-enriched peptides [Bornemann, V.; Chesnick, A. S.; Helms, G.; Moore, R. E.; Niemczura, W. P. 29th Experimental NMR Conference, Rochester, NY, April 17–21, 1988 (abstract 127)] and proteins [Stockman, B. J.; Westler, W. M.; Mooberry, E. S.; Markley, J. L. 29th Experimental NMR Conference, Rochester, NY, April 17–21, 1988 (abstract 122). Westler, W. M.; Kainosho, M.; Nagao, H.; Tomonaga, N.; Markley, J. L. 29th Experimental NMR Conference, Rochester, NY, April 17–21, 1988 (abstract 137). Oh, B. H.; Westler, W. M.; Darba, P.; Markley, J. L. 29th Experimental NMR Conference, Rochester, NY, April 17–21, 1988 (abstract 138)].

(2) [60% $^{13}C^0$ methionine, 60% u1-^{15}N]SSI was prepared essentially as reported previously[3,4] except that a hydrolyzate of [60% u1-^{15}N]yeast cells was used instead of an amino acid mixture. The concentration of this hydrolyzate in the culture fluid was 2% in terms of the amino acid mixture. Since the ratio of added DL-[99% atom 1-^{13}C]Met to [^{15}N]Met was approximately two, the expected level of ^{13}C enrichment is about 60%. (D-Met behaves essentially as L-Met, since racemization is very efficient for this amino acid.) The yield of labeled SSI from a 100-mL culture broth was 16 mg after the usual purification procedures.[3,4]

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